SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN

OMC Plant 2
Waukegan, Illinois

Pilot Study Test

WA No. 018-RICO-0528 / Contract EP-S5-06-01

December 2006

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OMC Plant 2
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RI/FS – Pilot Testing
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Date: December 2006

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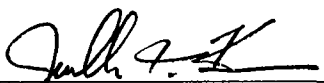

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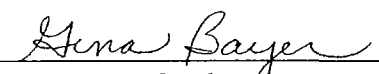

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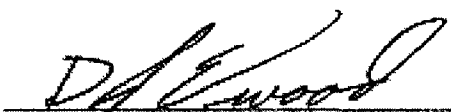

CT Laboratories Quality Assurance Manager (TBD)

Contents

Appendix

Tables

Abbreviations and Acronyms

bgs	below ground surface
CLP	contract laboratory program
CSU	Colorado State University
DCE	dichloroethene
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DPT	direct push technology
DQO	data quality objective
ELCR	excess lifetime cancer risk
EISB	enhanced in situ bioremediation
EOS™	edible oil substrate
FOP	field operating procedures
FS	feasibility study
ft^2	square feet
FTL	Field Team Leader
HPLC	high-performance liquid chromatography
HSA	hollow-stem auger
IEPA	Illinois Environmental Protection Agency
MCL	Maximum Contaminant Level
mL	milliliter
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
OMC	Outboard Marine Corporation
O&M	operations and maintenance
ORP	oxidation-reduction potential
OU	operable unit
OVA	organic vapor analysis
OVM	organic vapor meter

PCB	polychlorinated biphenyl
ppm	parts per million
PRG	Preliminary Remediation Goal
PVC	polyvinyl chloride
QA	quality assurance
QAPP	Quality Assurance Project Plant
QC	quality control
RD	remedial design
RI	Remedial Investigation
SDWA	Safe Drinking Water Act
SFSP	Supplemental Field Sampling Plan
SOP	standard operating procedure
SQAPP	Supplemental Quality Assurance Project Plan
TACO	Tiered Approach to Cleanup Objectives
TOC	total organic carbon
TCE	trichloroethylene
USEPA	U.S. Environmental Protection Agency
VOCs	volatile organic compound
ZVI	zero-valent iron

SECTION 1

Project Management

This *Supplemental Quality Assurance Project Plan* (SQAPP) presents the objectives, functional activities, and specific quality assurance (QA) and quality control (QC) activities for the pilot test to be conducted at the Outboard Marine Corporation (OMC) Plant 2 site in Waukegan, Illinois. This effort is being conducted in accordance with the Statement of Work (dated June 9, 2006) for Work Assignment No. 018-RICO-0528/Contract EP-S5-06-01.

CH2M HILL previously prepared a *Quality Assurance Project Plan* (QAPP, dated January 2005) for the remedial investigation (RI) that included the sampling of the building materials, soil and sediment, groundwater, and soil vapor. The investigation was designed to evaluate the impacts of OMC's historical operation and to evaluate the nature and extent of residual contamination in the different media. The site conceptual model, nature and extent of contamination and the assessment of risk to human health and the environment are presented in the *Remedial Investigation Report* (CH2M HILL, 2006a).

Potential groundwater alternatives were developed and evaluated in the draft *Feasibility Study Report* (FS) (CH2M HILL, 2006b). Pilot-scale testing will be conducted in order to evaluate the overall effectiveness of the proposed groundwater remedial alternatives and to refine the conceptual designs and cost estimates. This supplemental plan describes the investigation approach, data quality objectives, and analytical method requirements to be implemented during the pilot testing.

The environmental media sampling and analysis governed by this SQAPP involves the pilot testing of potential in situ groundwater treatment technologies. It has been developed as a supplement to the QAPP previously approved for the RI by the U.S. Environmental Protection Agency (USEPA), and discusses those elements that have been modified or are not included in the original QAPP. This supplemental plan references the original QAPP, where appropriate, and does not repeat information presented therein.

1.1 Problem Definition/Background Information

1.1.1 Background Information

This section provides a brief summary of the site description and project background. Detailed discussions of the site history, and physical and chemical characteristics are presented in the RI report (CH2M HILL, 2006a) and the draft FS report (CH2M HILL, 2006b).

The OMC Plant 2 site is at 100 East Seahorse Drive, Waukegan, Illinois and is the fourth operable unit (OU) of the OMC National Priorities List site. The 65-acre site includes a 1,036,000 square foot (ft^2) former manufacturing plant building (i.e., Plant 2) and several parking lot areas to the north and south of the building complex. The site includes two polychlorinated biphenyl (PCB) containment cells in which PCB-contaminated sediment (dredged from Waukegan Harbor in the early 1990s) and PCB-impacted soil are managed.

The cells (the "East Containment Cell" and the "West Containment Cell") are located north of Plant 2. OMC performed the harbor dredging work under a 1988 Consent Decree with USEPA and the Illinois Environmental Protection Agency (IEPA) that also required the long-term operations and maintenance (O & M) of the containment cells.

OMC designed, manufactured, and sold outboard marine engines, parts, and accessories to a worldwide market for many years. OMC Plant 2 was a main manufacturing facility for OMC—the major production lines used PCB-containing hydraulic and lubricating/cutting oils, chlorinated solvent-containing degreasing equipment, and smaller amounts of hydrofluoric acid, mercury, chromic acid, and other similar chemical compounds.

OMC filed for bankruptcy protection on December 22, 2000 and later abandoned the property after completing a limited removal action under USEPA oversight. In November 2001, the bankruptcy trustee filed a motion to abandon OMC Plant 2. USEPA conducted a site discovery inspection in spring 2002 to document the presence of numerous chemical compounds in OMC Plant 2 and support the allegation of imminent and substantial endangerment. Based on the findings, USEPA and the state of Illinois filed a joint objection to the abandonment and alleged that the site posed an imminent and substantial endangerment to public health and welfare and the environment. The bankruptcy trustee negotiated an emergency removal action scope of work with USEPA and IEPA that was approved by the court on July 17, 2002. The waste removal activities for the OMC Trust were completed in November 2002, and OMC Trust abandoned OMC Plant 2 property on December 10, 2002.

USEPA assumed control of building security and utilities on December 10, 2002 and planned further removal actions to clean up more of OMC Plant 2 in spring 2003. USEPA maintained electrical power to support O&M of the PCB containment cells until December 10, 2003, at which time the state took over the O&M of the cells.

A field investigation was conducted at the OMC Plant 2 site between January and June 2005 and identified the following potential environmental problems (CH2M HILL, 2006a):

- PCB-contaminated concrete floors, walls, and ceilings in the Old Die Cast, Parts Storage, and Metal Working Areas
- Chlorinated solvents in substantial quantities beneath the building
- A chlorinated solvent groundwater plume potentially migrating into Lake Michigan
- PCB-laden soils beneath the northern parking lot areas
- Pipe chases leading to the harbor and elsewhere containing oily residue laden with PCBs

Based on the data collected, potential alternatives were developed and evaluated in the draft FS report to address the contaminated building materials, soil and sediment, and groundwater (CH2M HILL, 2006b). The USEPA will make the determination regarding final selection of the remedial alternative(s) in the proposed plan.

1.1.2 Problem Definition

The technology screening and alternative development in the draft FS report identified in situ treatment (chemical reduction or enhanced bioremediation) as a viable response action

to address the volatile organic compound (VOC)-contaminated source zone areas, including the dense nonaqueous phase liquid (DNAPL) area, and the VOC groundwater plume at the OMC Plant 2 site. A pilot test was designed to collect the data needed to evaluate the overall effectiveness of the proposed in situ groundwater and DNAPL treatment technologies and to refine the conceptual design and cost estimate for the alternatives.

1.2 Project Description and Schedule

1.2.1 Project Description

The pilot test has been developed to acquire the additional information needed to determine if in situ treatment technologies can be used as the major component of the final groundwater remedy selected for the site. The pilot test entails the installation of additional monitoring wells, collection of groundwater samples, and injection or mixing of amendments to promote degradation of the VOC source zone areas. The information will be used to develop groundwater alternatives and to complete the FS.

The results of the RI indicate that the groundwater contamination is likely related to the use of chlorinated solvents, primarily trichloroethene (TCE), in past manufacturing operations at OMC Plant 2. The data indicate that the chlorinated "parent compound" in groundwater (TCE) was released to the subsurface during manufacturing operations and created "source zones." Source zones are portions of the aquifer that have particularly high dissolved phase TCE concentrations, and which may have residual DNAPL or high concentrations of adsorbed TCE that can continue to create and sustain dissolved phase plumes. The presence of the TCE degradation compounds (cis-1,2-dichloroethene [DCE] and vinyl chloride) and results of the natural attenuation parameters indicate that TCE is being degraded by anaerobic reductive dechlorination.

Pilot testing will be performed to evaluate the effectiveness of the two in situ technologies. Enhanced in situ bioremediation (EISB) will include the injection of soluble amendments (i.e., sodium lactate and an edible oil substrate [EOS™]) into two of the potential groundwater VOC source zone areas through injection wells. In situ soil mixing will use a patented amendment mixture of zero-valent iron (ZVI) and bentonite to treat an identified DNAPL area.

1.2.2 Project Schedule

The overall project schedule will be developed upon finalization of the work plan and the field sampling plan by USEPA.

1.3 Data Quality Objectives and Criteria for Measurement Data

Data quality objectives (DQOs) are qualitative and quantitative statements that clearly define the objectives of the project, define the most appropriate type of data, determine the appropriate procedures for data collection, and specify acceptable decision error limits that establish the quantity and quality of data needed for decisionmaking. The analytical methods and QC limits are summarized in Table 1.

The technical planning team developed project-specific DQOs in accordance with USEPA's *Guidance for Data Quality Objectives Process* (EPA QA/G-4). Proposed additions or changes to the requirements in the approved QAPP will be documented in a QAPP addendum and submitted to USEPA for review and approval. The results of the seven-step DQO Process for OMC Plant 2 (OU#4) are presented in the following sections.

1.3.1 Step 1: State the Problem

The purpose of the pilot test is to collect the data required to evaluate the effectiveness of the in situ groundwater technologies in treating the VOC-contaminated source zone areas and the DNAPL area, and to refine the conceptual design of the groundwater remedial alternatives and cost estimate in the FS. The identified problems for each of the data collection activities are discussed below.

1.3.1.1 DNAPL Delineation

Although in situ bioremediation methods have been found to be effective for reducing dissolved phase contamination, they have not yet been shown to be highly effective for directly remediating NAPL. The presence of DNAPL outside the building in the eastern portion of Area 2 requires more active remedial technologies than EISB. In situ soil mixing using a chemical reducing agent was selected to target this DNAPL area. To optimize the treatment of the DNAPL, the extent and thickness of the DNAPL in Area 2 must be accurately defined prior to the start of soil mixing activities.

1.3.1.2 EISB

The enhanced anaerobic bioremediation pilot test will involve the injection of the selected amendment into the shallow and deep intervals of the aquifer in two areas. An aqueous solution of the amendment will be prepared onsite and injected into a series of closely spaced, 2-inch-diameter injection wells. Based on the selected source zone treatment areas and the remedial technologies, the overall objectives for the pilot test are as follows:

- Evaluate the degree to which in situ treatment through substrate injection can reduce the concentrations of TCE and daughter products (cis-1,2-DCE and vinyl chloride) in the target source zone treatment areas and downgradient monitoring locations
- Determine the overall effectiveness of in situ treatment for achieving complete reduction of TCE to non-toxic degradation products (such as ethane or ethene)
- Monitor the duration that the injected substrates can maintain enhanced, relative to background, reducing conditions for in situ treatment
- Determine the radius of influence of the selected injection method

An additional objective of the pilot test is to examine the effectiveness of two different amendments—a soluble substrate (e.g., sodium lactate) and an EOS™. Both amendments work to enhance the natural reductive dechlorination processes in the aquifer. The composition and historical performance for both amendments indicate that either could be effectively used in the EISB remedial alternative. The testing will help to determine which amendment is more effective, under actual site conditions, in treating the site-related VOCs and should be recommended for use during the final remedy implementation.

1.3.1.3 In Situ Soil Mixing

Prior to completion of the design and implementation of the soil mixing pilot test, a bench-scale test will be conducted to evaluate the optimum dosage and source for the ZVI and potential amendments to control hydrogen gas production and enhance post-mixing soil strength. The bench-scale testing will be performed by Colorado State University (CSU), the patent holder for this technology. A description of CSU's proposed ZVI-clay treatability study will be provided in the Supplemental Field Sampling Plan.

In situ soil mixing pilot testing will be conducted in the area known to contain TCE DNAPL and located outside the building to treat the DNAPL identified during the RI. The overall objective of the soil mixing pilot test is to evaluate the reduction in the mass of DNAPL and mass flux of dissolved phase contamination from any remaining DNAPL.

1.3.2 Step 2: Identify the Decision

1.3.2.1 DNAPL Delineation

- Define the thickness and areal extent of the DNAPL area that will be treated using in situ soil mixing
- Determine the extent of groundwater impacts in the vicinity of the DNAPL

1.3.2.2 EISB

- Characterize the current (baseline) groundwater flow and water quality conditions of OMC Plant 2, especially in the vicinity of the source zone treatment areas
- Quantify changes in groundwater geochemistry and contaminant concentrations in response to the amendment injections
- Determine if favorable reducing conditions are being achieved and sustained to enhance or promote bioremediation of the chlorinated VOCs in the source zone areas and downgradient monitoring locations
- Determine overall temporal trends in groundwater quality
- Recommend the amendment and design of the EISB component of the overall groundwater remedy for the site

1.3.2.3 In Situ Soil Mixing

- Determine the optimum dosage and source for the ZVI and potential amendments to control hydrogen gas production and enhance post-mixing soil strength in order to complete the design of the pilot test
- Verify that the final ZVI concentrations meet design parameters (i.e., the target iron ratio)
- Determine the effect of the mixing on soil and pore water in the mixing zone and groundwater in downgradient monitoring locations
- Recommend soil mixing if it would provide effective treatment of the DNAPL if other DNAPL areas are found during the building demolition or subsequent site remediation

1.3.3 Step 3: Identify the Inputs to the Decision

This section describes how the project objectives will be met by proposed sample collection and analyses. A summary of the sample collection activities is presented in Table 2.

1.3.3.1 DNAPL Delineation

This focused investigation will include the collection of groundwater grab samples from the base of the aquifer (about 30 feet below ground surface [bgs]) at an estimated 24 boring locations. Initially, grab samples will be collected from eight borings located at a 25-foot radius from the soil boring (SO-057) where DNAPL was encountered during the RI. Discreet groundwater samples and soil samples will be collected, field screened (total organic vapor measurements), and examined for visual and olfactory evidence of mobile and/or residual DNAPL. Samples will not be sent for laboratory analysis. Subsequent sets of eight borings will be stepped out or moved in at 10-foot increments based on the presence/absence of DNAPL in the soil/groundwater samples.

Three monitoring wells nests will be installed to monitor changes in groundwater conditions resulting from the soil mixing. The new monitoring wells will be included in the EISB monitoring program.

1.3.3.2 EISB

Prior to the start of the pilot testing, water level measurements and groundwater samples will be collected from a total of 16 new and 58 existing monitoring wells. The groundwater samples will be analyzed for the parameters listed in Table 3. The data collected will be used to establish baseline groundwater flow and water quality conditions (including extent of DNAPL) prior to the start of the pilot test.

Following the initial injection, performance monitoring events will be conducted at designated intervals to quantify changes in groundwater geochemistry and contaminant concentrations. The post-injection monitoring will consist of primary and secondary performance monitoring events that will begin 30 days post injection (Table 4). For primary and secondary post-injection monitoring, groundwater samples will be collected from 20 monitoring wells (16 new and 4 existing monitoring wells). Secondary monitoring events will be performed every 30 days and will include pH, temperature, turbidity, oxygen reduction potential, specific conductance, dissolved oxygen (DO), and total organic carbon (TOC). Primary monitoring events will be performed every 90 days post injection and will include the parameters listed in Table 3. Performance monitoring will continue for approximately 18 months resulting in 6 secondary and 4 primary monitoring events. The timeline for sampling is estimated and may be modified based on the results of prior sampling events or field observations.

An annual monitoring event will be conducted to evaluate overall temporal trends in the groundwater quality. Groundwater samples will be collected using low-flow purge techniques from the 16 new and 58 existing monitoring wells and analyzed for the parameters listed in Table 3. The actual number of existing wells to be sampled may be reduced based on the results of the baseline groundwater sampling.

1.3.3.3 Soil Mixing

A bench scale test will be conducted by CSU to optimize the effectiveness of the in situ soil mixing. Approximately 200 pounds of soil, 1 gallon of groundwater, and 80 milliliters (mL) of DNAPL will be collected using direct push technology (DPT) methods during the DNAPL delineation activities and sent to CSU for use in the bench testing.

Ten soil samples will be collected during and after soil mixing from within the mixing zone and around the perimeter. Soil samples from within the mixing zone will be analyzed in the field for iron to confirm that the final ZVI concentrations meet design parameters (i.e., the target iron ratio). Soil samples will also be analyzed for VOCs to monitor the effect of the mixing and serve as a baseline for comparison of soil sample results at intervals following treatment.

In addition, three suction lysimeters will be installed in the soil mixing area to sample pore water for VOCs immediately following soil mixing and at intervals following treatment. Groundwater samples will also be collected using low flow purge techniques from the three monitoring wells in the vicinity of the mixing zone and analyzed for parameters listed in Table 5. Two rounds of groundwater sampling will be conducted concurrent with the EISB post-injection monitoring.

1.3.4 Step 4: Define the Study Boundaries

The limits of the OMC Plant 2 study area consists of about 65 acres, upon which a 1,036,000 ft^2 former manufacturing plant building and several parking lot areas to the north and south of the building complex are situated. To the east of the Plant 2 site is Lake Michigan and to the south is Larsen Marine and Waukegan Harbor.

1.3.4.1 DNAPL Delineation

The DNAPL delineation will include the area located within a 50-foot radius from the soil boring (SO-057) where DNAPL was encountered during the RI. Groundwater grab samples collected from offset borings installed 50 feet north, south, east, and west of the SO-057 did not indicate the presence of DNAPL. The initial set of borings will be installed 25 feet from the original boring (SO-057) where DNAPL was observed. Subsequent borings will be stepped out or moved in at 10-foot increments based on the presence or absence of DNAPL in the soil/groundwater samples.

1.3.4.2 EISB

The baseline groundwater monitoring events will include a total of 75 monitoring wells across the site:

- Existing monitoring wells—58 wells
- New monitoring wells—16 wells

Primary and secondary performance monitoring will include the following:

- Existing monitoring wells—4 wells (2 wells in Area 2 and 2 wells in Area 4)
- New monitoring wells—16 wells (10 wells in Area 2 and 6 wells in Area 4)

The annual groundwater monitoring events will include a maximum total of 75 monitoring wells across the site:

- Existing monitoring wells – 58 wells (the actual number may be reduced based on the results of the baseline groundwater monitoring)
- New monitoring wells – 16 wells

1.3.4.3 Soil Mixing

The sampling locations for the soil mixing will include the following:

- Soil, groundwater, and DNAPL samples from within the DNAPL area for the bench-scale testing
- Soil samples from within and in the vicinity of the mixing zone
- Pore water samples from within the mixing zone
- Groundwater samples from monitoring wells of the mixing zone

1.3.5 Step 5: Develop a Decision Rule

Chemicals of concern are defined as those most likely to contribute a risk as a result of exposure. The results of the field investigation, conducted between January and June 2005, indicate that the groundwater contamination is mainly related to the use of chlorinated solvents, primarily TCE, in past manufacturing operations at OMC Plant 2. The presence of the TCE degradation compounds (cis-1,2-DCE and vinyl chloride) and results of the natural attenuation parameters indicate that TCE is being degraded by anaerobic reductive dechlorination.

Based on the results of the previous investigations and the risk evaluations conducted, the primary contaminants in the groundwater include VOC (primarily, the chlorinated VOCs). Groundwater samples will also be analyzed to determine if the in situ treatment of the source zone areas have enhanced the natural reductive dechlorination processes occurring in the aquifer. The list of monitoring parameters and the rationale for the analysis are presented in Table 3.

The RI indicates that chlorinated VOCs are present in the groundwater at levels greater than the Safe Drinking Water Act (SDWA) federal Maximum Contaminant Levels (MCLs), USEPA Region 9's Preliminary Remediation Goals (PRGs) and the State of Illinois Tier 1 Remediation Objectives in 35 IAC Subtitle G, Chapter I, Subchapter f, Part 742, Appendix B (TACO). In the feasibility study (FS), the significantly lower USEPA Region 9 PRGs were selected as the remediation goal for groundwater so that the cumulative risk from ingestion of groundwater does not exceed the 1×10^{-4} excess lifetime cancer risk (ELCR) value mandated by the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The data generated during the pilot test and associated analytical program will be used to achieve these remediation goals. The USEPA Region 9 PRGs and Tier 1 Remediation Goals for the VOCs in water are presented in Table 1.

1.3.6 Step 6: Specify Limits on Decision Errors

The probability of sampling and measurement errors at any site under investigation necessitates the development of sampling guidelines and the collection of quality control samples. Field errors are minimized by having each member of the field team follow the same field operating procedures (FOPs) for sampling. Sampling techniques are discussed in detail in the FSP. Quality control (QC) samples are used to verify the accuracy and precision of the data. When a QC sample is outside the established control limits, the data will be qualified and field corrective action implemented when applicable (such as when field duplicates are outside established control limits).

Field data, such as groundwater pH, temperature, specific conductance, DO, and oxidation-reduction potential (ORP), will not be subject to data validation.

1.3.7 Step 7: Optimizing the Design

The sampling design objectives are to provide the information to define the DNAPL boundaries, verify groundwater flow and water quality conditions, and assess the effectiveness of the in situ treatment technologies to refine the conceptual design of the groundwater remedial alternative and cost estimate in the FS.

1.3.8 Measurement Performance Criteria

The measurement performance criteria are checked on several levels:

- Built-in QC standards
- Senior review
- Management controls

The measurement data must abide by specific QC standards. Data that do not meet these standards are qualified accordingly. The analytical data and the QC results are checked by the bench chemist, the Laboratory's QA Manager, CH2M HILL's project chemist, and the USEPA's data validator.

CH2M HILL staff members with relevant technical experience will review all documents that pertain to the project's quality standards. The Field Team Leader (FTL) will supervise activities to assess whether FOPs are being followed during field sampling activities. Section 3 describes the specific QC checks and corrective action measures.

SECTION 2

Data Generation and Acquisition

This section describes the procedures for acquiring, collecting, handling, measuring, and managing data in support of this sampling activity. Only sections that are different from the original QAPP (CH2M HILL, 2004) are addressed in this document.

2.1 Sampling Process Design

The sampling locations and sample quantity were chosen to best fulfill the project objectives stated in Step 2 of the DQO process. The sampling design consists of three components: the DNAPL delineation, EISB, and in situ soil mixing. For more information on proposed sample locations and quantities, refer to Table 2 of this SQAPP (see Section 1.3.3 and Section 2 of the *Supplemental Field Sampling Plan* [SFSP, CH2M HILL, 2006]).

2.1.1 DNAPL Delineation

Soil and groundwater grab samples will be collected from an estimated 24 borings to delineate the DNAPL area. The initial eight soil borings will be installed 25 feet from the soil boring (SO-057) where DNAPL was detected during the RI. Additional boring locations will be offset based on the presence/absence of DNAPL in the soil/groundwater samples.

Soil samples will be collected continuously using DPT (e.g., Geoprobe®) methods from the ground surface to the top of the till (estimated to be 30 feet bgs). The soil samples will be logged, field screened using an organic vapor meter (OVM), and examined for visual indications of mobile and/or residual DNAPL. A groundwater grab sample will also be collected at each boring from the base of the aquifer and visually examined for the presence of DNAPL. Samples will not be collected for laboratory analysis.

Groundwater monitoring well nests will be installed at an estimated three locations to monitor changes in groundwater quality due to the soil mixing activities. Each well nest will consist of a shallow well installed at the water table (well depth of 15 feet) and a deep well installed at the top of the till (well depth of about 30 feet). The 2-inch monitoring wells will be installed using hollow-stem auger (HSA) techniques, constructed of polyvinyl chloride (PVC) casing and well screens and developed in accordance with the FOPs. The monitoring wells will be sampled using the low-flow sampling methods prior to and after mixing and analyzed for VOCs, TOC, volatile fatty acids, and natural attenuation parameters (see Table 3). These new monitoring wells will be included in the overall baseline groundwater sampling event and with the EISB post-injection performance monitoring program.

2.1.2 EISB

Groundwater samples will be collected from the 16 new monitoring wells and the 58 previously installed monitoring wells to establish baseline groundwater conditions prior to the start of the pilot testing. Groundwater samples will be collected using low-flow methods and analyzed for the parameters presented in Table 3.

Prior to sampling, groundwater levels will be measured with an electronic water level indicator. In addition, an oil-water interface probe will be lowered to the bottom of the well to check for the presence or absence of NAPL in monitoring wells and to measure the total depth of the well. The well depth will be used to calculate the required purge volumes and assess the amount of solids collecting in the well.

Primary and secondary performance groundwater monitoring will be conducted after the injections to quantify changes in groundwater geochemistry and contaminant concentrations. Groundwater samples from 20 monitoring wells (16 new and 4 existing wells) will be collected using low-flow purge techniques. The groundwater samples for primary performance monitoring events will include analyses of all parameters listed in Table 3. The secondary performance monitoring events will only include analyses for field parameters (ORP, pH, DO, temperature, turbidity, and conductivity) and TOC. Field parameters will be collected during well purging using field instruments. Visual indications (color) of substrate migration will also be noted.

An annual monitoring event will be conducted to evaluate overall temporal trends in the groundwater quality. Groundwater samples will be collected using low-flow purge techniques from the 75 new and existing monitoring wells and analyzed for the parameters listed in Table 3. The actual number on existing monitoring wells may be revised based on the results of the baseline groundwater sampling.

2.1.3 Soil Mixing

2.1.3.1 Bench-Scale Testing

The bench-scale test will be conducted by CSU to optimize the effectiveness of the in situ soil mixing. The objectives of the bench test are to collect site-specific information on the optimum dosage and source of the ZVI, and potential amendments to control hydrogen gas production and enhance post-mixing soil strength. Approximately 200 pounds of soil, 1 gallon of groundwater, and 80 mL of DNAPL will be collected using DPT methods during the DNAPL delineation activities and sent to CSU for use in the testing. The proposed bench test will consist of the following:

- Soil will be visually logged and monitored via organic vapor analyzer (OVA). Samples with elevated OVA readings will be screened for the presence of DNAPL using Sudan IV and an ultraviolet light. After logging, the soil samples will be combined into a single composite sample.
- The composite soil sample will be mixed with site water, spiked with the DNAPL, and homogenized prior to filling the study columns.
- A grout mixture with predetermined amounts of reactive media (granular iron), stabilizing agents (bentonite), and other ingredients (sodium bicarbonate or fly ash) will be mixed with the spiked site soil in each column.
- Soil samples will be collected immediately after mixing; subsequent samples will be collected after approximate reaction times of 3, 7, 28, and 56 days and analyzed for water content and chloride concentration. During the experiment, the volume of gas produced in each column will also be monitored.

- At the end of the experiment (approximately 56 days), a portion of three select columns will be measured for compressive strength (American Society for Testing and Materials D4219-02).

The description of CSU's proposed ZVI-clay treatability study is provided in Appendix A of the SFSP.

2.1.3.2 Monitoring for the Soil Mixing Pilot Test

During and after the soil mixing, soil samples will be collected from the mixing zone and around the perimeter to quantify homogeneous amendment distribution throughout the mixing zone, concentrations of the amendment in the mixing zone, changes in groundwater geochemistry, and changes in contaminant concentrations. An estimated 10 soil samples from within the mixing zone will be analyzed in the field for iron to confirm that the final ZVI concentrations meet design parameters (i.e., the target iron ratio). Soil samples will also be analyzed for VOCs to monitor the effect of the mixing and serve as a baseline for comparison of soil sample results at intervals following treatment.

Suction lysimeters will be installed at three locations within the mixing zone to collect groundwater samples immediately following the mixing and at intervals following treatment. Two rounds of groundwater samples collected concurrent with the EISB post injection monitoring will be analyzed for VOCs.

Groundwater samples will also be collected using low-flow purge techniques from the monitoring wells in the vicinity of the mixing zone. Post treatment sampling has been designed to monitor for any increasing dissolved phase concentrations or changes in groundwater conditions resulting from disturbance of the DNAPL. Table 5 presents a summary of the performance confirmation sampling parameters.

2.2 Sampling Method Requirements

The FOPs for the field sampling method and decontamination procedures are provided in the FSP (CH2M HILL, 2004). The procedures for the installation and sampling of the suction lysimeters will be provided in *FOP 22 Suction Lysimeter Installation and Pore Water Sample Collection Procedure* in the SFSP.

Before sampling at a station, reusable (i.e., nondedicated) sampling equipment will be scrubbed with Alconox, rinsed with distilled water, then rinsed with methanol, again rinsed with distilled water, and air-dried. Large sampling equipment will be washed with a high-pressure water wash using a brush, as necessary, to remove any particles. Field blanks will be collected by passing high-performance liquid chromatography (HPLC)-grade laboratory water over decontaminated sampling equipment. The field blanks will then be analyzed for the same parameters as the field samples to assess the effectiveness of the decontamination procedures.

2.3 Sample Handling and Custody Requirements

Table 6 summarizes the sample preservation and holding requirements.

Corrective actions will be taken as soon as a problem is identified. Such actions may include discontinuing the use of a specific bottle lot, contacting the bottle suppliers for retesting the representative bottle from a suspect lot, resampling suspect samples, validating the data, taking into account that the contaminants could be introduced by the laboratory (e.g., common lab solvents, sample handling artifacts) as a bottle QC problem, and determining whether the bottles and data are usable.

The sample identification system, packaging, and custody requirements are as described in the QAPP (CH2M HILL, January 2005).

2.4 Analytical Method Requirements

Once the samples have been properly collected and documented, they will be sent to a USEPA contract laboratory program (CLP) laboratory for analysis. Certain analyses that cannot be performed by CLP laboratories will be sent to CT Laboratories, an offsite laboratory subcontracted by CH2M HILL for analysis located in Baraboo, Wisconsin. Analytical method requirements and level of quantification were received by CT Laboratories as part of the procurement process.

Table 1 lists the required methodologies and the quantification limits for the analyses to be performed during the pilot study test.

The laboratory will use analytical standard operating procedures (SOPs) to ensure the submitted samples are accurate and analyzed precisely. The analytical SOPs reflect the requirements of the stated methods, while including internal QC criteria. The QC criteria used during the analyses will be those stated within the analytical SOPs obtained from CT Laboratories and included in Appendix A.

SECTION 3

Assessment/Oversight

See Section 3 of the original QAPP.

SECTION 4

Data Validation and Usability

4.1 Validation and Verification Methods

Data collected as part of this investigation will be consistent with this supplemental QAPP. USEPA will perform data validation for CLP-generated data in a manner consistent with the USEPA's *CLP National Functional Guidelines for Superfund Organic Methods Data Review* (January 2005), and *USEPA's CLP National Functional Guidelines for Inorganic Data Review (October 2004)*. Criteria for assessment (for example, DQOs contained in these documents) are superseded by the laboratory Statement of Work. Sample results will then be assigned a degree of usability based upon overall data quality. The CH2M HILL team will evaluate the USEPA's data validation results. This evaluation will assess how the data, as qualified by the data validation, can be used on the project.

CH2M HILL will perform the data evaluation on the subcontracted laboratory results for all non-CLP analytical results including TOC volatile fatty acids, the natural attenuation parameters, and field parameters. The data validation will be conducted to assess the quality of the data, the defensibility of the data, and to check the chain of custody. The CH2M HILL chemist will review the validated analytical results against the DQOs to determine if the data are acceptable. The validation procedures to be undertaken by CH2M HILL staff are described in the QAPP (CH2M HILL, 2004).

4.2 Reconciliation with Data Quality Objectives

The final activity of the data validation process is to assess whether the data fulfill the objectives for the project. The final results, as adjusted for the findings of any data validation/data evaluation, will be checked against the DQOs. The data acquired from the pilot study test activities should fulfill the project objectives, which are to provide the information necessary for design of the full-scale processes and to resolve engineering design decisions.

SECTION 5

References

CH2M HILL. 2006a. *Remedial Investigation Report, OMC Plant 2, Waukegan, Illinois.* April.

CH2M HILL. 2006b. *Draft Feasibility Study Report, OMC Plant 2, Waukegan, Illinois.* May.

CH2M HILL. 2006c. OMC Plant 2 (OU#4) Groundwater Treatment Pilot Study. Technical Memorandum to Kevin Adler/USEPA, dated May 18.

CH2M HILL. 2005. *Quality Assurance Project Plan, OMC Plant 2, Waukegan, Illinois.* January.

CH2M HILL. 2004. *Field Sampling Plan, OMC Plant 2, Waukegan Illinois.* November.

U.S. Environmental Protection Agency. 2005. *Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review.* OSWER 9240.1-44. EPA-540-R-04-001.

U.S. Environmental Protection Agency. 2004. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review.* OSWER 9240.1-45/EPA 540-R-04-004

Tables

TABLE 1
Groundwater Analytical Objectives
OMC Plant 2

Parameter - TCL VOCs (CLP SOW SOM01.1)	CAS No.	USEPA Region 9 PRG Tap Water (µg/L)	IEPA Tier 1 TACO Groundwater Class 1 (µg/L)	Achievable Laboratory MDLs[a]	Contract Required Quantitation Limit (CRQL) (µg/L)
Acetone	67-64-1	5475	700		5.0
Benzene	71-43-2	0.35	5.0		0.5
Bromodichloromethane	75-27-4	0.18	0.2		0.5
Bromoform (tribromomethane)	75-25-2	8.51	1		0.5
Bromomethane (Methyl bromide)	74-83-9	8.66	---		0.5
Bromochloromethane	74-97-5	---	---		0.5
2-Butanone (Methyl ethyl ketone)	78-93-3	6968	---		5.0
Carbon disulfide	75-15-0	1043	700		0.5
Carbon tetrachloride	56-23-5	0.17	5.0		0.5
Chlorobenzene	108-90-7	106	100		0.5
Chloroethane	75-00-3	4.64	---		0.5
Chloroform	67-66-3	0.17	0.2		0.5
Cyclohexane	110-82-7	10342	---		0.5
Chloromethane (methyl chloride)	74-87-3	158	---		0.5
Dibromochloromethane	124-48-1	0.13	---		0.5
Dichlorofluoromethane	75-43-4	---	---		0.5
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	0.05	0.2		0.5
1,2-Dichlorobenzene	95-50-1	370	600		0.5
1,3-Dichlorobenzene	541-73-1	183	---		0.5
1,4-Dichlorobenzene	106-46-7	0.50	75		0.5
1,1-Dichloroethane	75-34-3	811	700		0.5
1,2-Dichloroethane (EDC)	107-06-2	0.12	5.0		0.5
1,2-Dibromoethane (EDB)	106-93-4	0.01	---		0.5
1,1-Dichloroethylene	75-35-4	339	7.0		0.5
1,2-Dichloroethylene (cis)	156-59-2	61	70		0.5
1,3-Dichloropropene (cis)	10061-01-5	---	---		0.5
1,2-Dichloroethylene (trans)	156-60-5	122	100		0.5
1,3-Dichloropropane	142-28-9	122	---		0.5
1,2-Dichloropropane	78-87-5	0.16	5.0		0.5
Ethylbenzene	100-41-4	1340	700		0.5
2-hexanone	591-78-6	---	---		5.0
Methyl isobutyl ketone	108-10-1	1993	---		5.0
Methylene chloride	75-09-2	4.28	5.0		0.5
Methylcyclohexane	108-87-2	5217	---		0.5
Methyl tertbutyl ether (MTBE)	1634-04-4	11.00	---		0.5
Methyl acetate	79-20-9	6083	---		0.5
Isopropylbenzene (Cumene)	98-82-8	658	---		0.5
1,1,2,2-Tetrachloroethane	79-34-5	0.06	---		0.5
1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	59180	---		0.5
Styrene	100-42-5	1641	---		0.5
Tetrachloroethylene (PCE)	127-18-4	0.10	5.0		0.5
Toluene	108-88-3	723	1000		0.5
Trichlorofluoromethane	75-69-4	1288	---		0.5
1,2,4-Trichlorobenzene	120-82-1	7.16	70		0.5
1,2,3-Trichlorobenzene	87-61-6	---	---		0.5
1,1,1-Trichloroethane	71-55-6	3172	200		0.5
1,1,2-Trichloroethane	79-00-5	0.20	5.0		0.5
Trichloroethylene (TCE)	79-01-6	0.03	5.0		0.5
Vinyl chloride (child/adult)+++	75-01-4	0.02	2.0		0.5
Xylenes	1330-20-7	206	10,000		0.5

"---" indicates no limit identified

[a]Analyses to be performed by a CLP laboratory do not have Achievable Laboratory Method Detection Limits (MDLs) listed because they are laboratory specific and the CLP laboratory to run the analyses will not be selected until approximately a week before samples are collected.

TABLE 2
Summary of Sample Collection Activities
OMC Plant 2

Task	Activity	Media	Collection Method	Number of Sampling Locations	Sample Depth	Number of Samples[a]	Analysis[b]	Rationale of Selection of Sampling Location
DNAPL Delineation	DNAPL Delineation	Soil or Discrete Groundwater Grab	Direct push method	24	Bottom of the aquifer	24	Visual and field screening No laboratory analysis	Initial borings will be located at a 25-foot radius from the soil boring that DNAPL was encountered in the RI. Subsequent sets of 8 borings will be stepped out or moved in at 10-foot intervals based on the presence/absence of DNAPL in soil and groundwater samples.
	Groundwater Sampling	Groundwater	Low flow sampling	6	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	6	TCL VOCs Field Analyses[c] Natural Attenuation Parameters[d] Total Organic Carbon Volatile Fatty Acids	Three new wells will be installed to evaluate impacts to groundwater downgradient of DNAPL area. These wells will be sampled as part of the EISB monitoring activities.
EISB	Baseline Monitoring	Groundwater	Low flow sampling	58 existing wells 16 new wells	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	74	TCL VOCs Field Analyses[c] Natural Attenuation Parameters[d] Total Organic Carbon Volatile Fatty Acids	Monitor site-wide groundwater flow and water quality conditions.
	Secondary Performance Monitoring	Groundwater	Low flow sampling	4 existing wells 16 new wells	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	20	Field Analyses[c] Total Organic Carbon	Monitor changes in groundwater geochemistry in source and downgradient areas.
	Primary Performance Monitoring	Groundwater	Low flow sampling	4 existing wells 16 new wells	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	20	TCL VOCs Field Analyses[c] Natural Attenuation Parameters[d] Total Organic Carbon Volatile Fatty Acids	Monitor changes in groundwater geochemistry and contaminant concentrations in source and downgradient areas.
	Annual Monitoring	Groundwater	Low flow sampling	58 existing wells 16 new wells	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	74	TCL VOCs Field Analyses[c] Natural Attenuation Parameters[d] Total Organic Carbon Volatile Fatty Acids	Monitor site-wide groundwater flow and water quality conditions.
In Situ Soil Mixing	Implementation	Soil	Direct push method	10	Within mixing zone	10	Iron (field measurement) TCL VOCs	Confirm that the final ZVI concentrations meet design parameters. Monitor effect of mixing within the treatment zone.
	Performance Monitoring	Pore Water	Low flow sampling	3 suction lysimeters	Within mixing zone	3	TCL VOCs	Monitor effect of mixing within the treatment zone.
	Performance Monitoring	Groundwater	Low flow sampling	6 new wells	Water table wells (0 to 10 feet) Deep wells (20 to 30 feet)	6	TCL VOCs Field Analyses[c] Chloride Iron	Monitor effect of mixing within the treatment zone. This sampling will be conducted concurrent with the EISB post-injection sampling.

[a]Does not include quality control samples.
[b]The parameter list for each of the analyses identified are provided in Table 1.
[c]Field analysis includes: water levels, temperature, pH, specific conductance, dissolved oxygen, oxidation-reduction potential, and turbidity.
[d]Natural attenuation parameters include: total alkalinity, nitrate, nitrite, chloride, ferrous iron, dissolved manganese, sulfate, sulfide, methane, ethane, ethene

TABLE 3
List of EISB Monitoring Parameters and Rationale

Parameter	Method	Reason for Monitoring
Water Level	Field measurement, taken using a water level indicator.	Provides quantitative indication that injection fluids are reaching the monitoring well. Also used to determine the well volume for purging.
Turbidity	Field measurement	Typically used for well purge stabilization parameter.
Temperature	Field measurement.	Typically used for well purge stabilization parameter.
Specific Conductance	Field measurement	Typically used for well purge stabilization parameter.
Oxygen Reduction Potential (ORP)	Field measurement	To assess the degree to which the injection or mixing is enhancing the reducing conditions and whether groundwater conditions are optimal for biodegradation (ORP values less than -100 millivolts [mV]).
Dissolved Oxygen (DO)	Field measurement	To assess the degree to which the injection or mixing is enhancing the reducing conditions and whether groundwater conditions are optimal for biodegradation (DO values less than 0.5 mg/L).
pH	Field measurement	To assess the degree to which the injection or mixing is enhancing the reducing conditions. Ideal range for dechlorination bacteria is 5 to 9. Also a well purge stabilization parameter.
Alkalinity	SM 2320-B or EPA 300 Series	Indicator of biodegradation and the buffering capacity of the aquifer.
Nitrate/Nitrite	SW9056 or EPA 300 Series	Nitrate is an alternate electron acceptor for microbial respiration in the absence of oxygen. Nitrate levels less than 1.0 mg/L are desirable for anaerobic dechlorination.
VOCs	SOM01.1 (water and soil samples)	The chemicals of concern. A decrease in concentration of parent compounds will provide a direct indication that the biodegradation reactions are occurring.
Chloride	SW 846-9056 or EPA 300 Series	Chloride ions are produced by anaerobic dechlorination and may be used as secondary indication of the occurrence of reactions.
Ferrous Iron	SW 846-6010B (water samples) Field measurement (soil samples)	Ferric iron is an alternate electron acceptor for microbial respiration in the absence of oxygen and nitrate; ferrous iron is produced by the reduction of ferric iron. This analysis provides information about the degree to which iron reduction processes are occurring in the aquifer. Soil samples will be analyzed using field measurements to confirm the target ratio of iron in the soil mixing area.
Dissolved Manganese	SW846 6010B	Dissolved manganese (Mn^{2+}) is produced by the reduction of Mn^{4+} in a process similar to iron reduction. This analysis provides information about the degree to which manganese reduction processes are occurring in the aquifer.
Sulfate	EPA 300 Series	Sulfate is an alternate electron acceptor for microbial respiration in the absence of oxygen, nitrate, and ferric iron. Sulfate levels of less than 20 mg/L are desirable, but not

TABLE 3
List of EISB Monitoring Parameters and Rationale

Parameter	Method	Reason for Monitoring
		required, for anaerobic dechlorination.
Sulfide	EPA 300 Series	Sulfide is produced during reduction of sulfate. Its presence indicates that sulfate reduction is occurring.
Methane/Ethane/ Ethene	RSK 175	Methane, ethane, and ethane are the final byproducts of reductive dechlorination of chlorinated solvents.
Volatile Fatty Acids (VFAs)	Ion chromatography	VFAs are produced as the microbial community ferments the EISB amendments, providing evidence of enhanced biological activity.
Total Organic Carbon (TOC)	SW 9060 or EPA 400 Series	Indicator of the natural organic carbon present at the site during baseline sampling and as an indicator of the substrate distribution during performance monitoring.

TABLE 4
Approximate Sampling Schedule for Post-Injection Performance Monitoring
OMC Plant 2

Sampling Event	Number of Days Post-injection
Injection	0
Secondary Monitoring	30
Secondary Monitoring	60
Primary Monitoring	90
Injection	0
Secondary Monitoring	30
Secondary Monitoring	60
Primary Monitoring	90

TABLE 5
List of Soil Mixing Performance Sampling and Monitoring Parameters
OMC Plant 2

Parameter	Method	Rationale for Monitoring
Water Level	Field measurement, taken using a water level indicator	Provides quantitative indication that injection fluids are reaching the monitoring well. Also used to determine the well volume for well purging.
Turbidity	Field measurement	Typically used for well purge stabilization parameter.
Temperature	Field measurement.	Typically used for well purge stabilization parameter.
Specific Conductance	Field measurement	Typically used for well purge stabilization parameter.
ORP	Field measurement	To assess the degree to which the mixing is enhancing the reducing conditions and whether groundwater conditions are optimal for biodegradation (ORP values less than -100 mV).
DO	Field measurement	To assess the degree to which the mixing is enhancing the reducing conditions and whether groundwater conditions are optimal for biodegradation (DO values less than 0.5 mg/L).
pH	Field measurement	To assess the degree to which the mixing is enhancing the reducing conditions. Ideal range for dechlorination bacteria is 5 to 9. Also a well purge stabilization parameter.
VOCs	SOM01.1 (water and soil samples)	The chemicals of concern. A decrease in concentration of parent compounds will provide a direct indication that the reduction reactions are being effective.
Chloride	SW 846-9056 or EPA 300 Series	Chloride ions are produced by anaerobic dechlorination and may be used as secondary indication of the occurrence of reactions.
Total Iron	Field measurement	Soil samples will be collected to confirm the target ratio of iron.

TABLE 6
Sample Containers, Preservatives, and Holding Times
OMC Plant 2

Analysis	Method[a, b]	Container	Preservation/ Storage	Maximum Hold Time
Groundwater				
TCL VOCs	SOM01.1	Three 40-mL VOA vials	HCl to pH ≤ 2, 4°C	7 days to extraction, 40 days from extraction to analysis
Total Alkalinity	EPA 300 Series	100-mL poly	4°C	14 days
Nitrate	SW9056/EPA 300 series	100-mL poly	4°C	48 hours
Nitrite	EPA 300 series	100-mL poly	4°C	48 hours
Chloride	SW 9056 or EPA 300 series	250-mL poly	4°C	28 days
Ferrous Iron	SW 846-6010B	glass	4°C	Immediately
Dissolved Manganese	SW 846 6010B	250-mL poly	HNO_3 to pH <2, 4°C	180 days
Sulfate	SW 9056 or EPA 300 series	250-mL poly	4°C	28 days
Sulfide	EPA 300 series	500-mL poly	4°C, Zn acetate, NaOH to pH>9	7 days
Methane/Ethene/Ethane	RSK 175	Three 40mL VOA vials	4°C	14 days
Volatile Fatty Acids	SW 9056	Three 40mL VOA vials	4°C	7 days
TOC	SW-846 9060	100-mL poly	HCl to pH <2, 4°C	28 days
Soil				
TCL VOCs	SOM01.1	Three 5-gram (g) Encore Samplers plus one 4-oounce (oz) glass	4°C	48 hours
Investigation-Derived Waste (characterization sampling)				
Soil				
TCLP VOCs	SW 846 1311/8260B	One 4-oz glass – no head space (must have 5g of soil)	4°C	14 days
Groundwater				
TCL VOCs	SOM01.1	Three 40-mL VOA vials	HCl to pH ≤ 2, 4°C	7 days to extraction, 40 days from extraction to analysis

[a]Identified method may be modified based on quantitation limits to achieve USEPA Region 9 Preliminary Remediation Goals or Illinois TACO Tier 1 remediation objectives.
[b]CLP method listed or equivalent

Appendix A
Analytical Standard Operating Procedures

CT Laboratories.

Title: **Ion Chromatography analysis of Volatile Fatty Acids**

SOP Number: **CC-VFA**

Prepared by: _____
Date

Technical Review by: _____
Date

Reviewed by: _____
Quality Assurance ***Date***

_____
Laboratory Director ***Date***

SOP Manual Control Number:_____

1.0 SCOPE AND APPLICATION

1.1 This method covers the sequential determination of the Volatile Fatty Acids: acetic, butyric, formic, lactic, propionic and pyruvic acids in all water samples. Other volatile fatty acids may be ammeanable to this procedure.

2.0 METHOD SUMMARY

2.1 A small volume of water is injected into an ion chromatograph to flush and fill a 50uL constant volume sample loop. The sample is then injected into a stream of heptafluorobutyric acid eluent.

2.2 The sample is pumped through an ion exchange column and into a conductivity detector. The column is packed with a fully sulfonated styrene/divinylbenzene resin. Ions are separated into discrete bands based on Donnan exclusion, steric exclusion and adsorption partition of the resin. The last column is a regenerating suppressor column that uses a cation regenerant solution. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

3.1 Calibration Blank (CB)—A volume of reagent water fortified with the same matrix as the calibration standards. It is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 20 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration, or possible analyte carry-over. Control criteria consist of the absolute value being less than the MDL for a given analyte.

3.2 Calibration standards (ICAL)—A solution prepared from the stock standard solutions. The ICAL solutions are used to calibrate the instrument. Acceptance of the calibration requires a correlation coefficient of 0.995 or better. No samples will be analyzed without acceptable calibration.

3.2 Laboratory Control Standard (LCS) -- A mid-range standard prepared from a source different from that used for calibration standards. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control. The retention times of the analytes in the LCS must be within 10% of the retention time of the analytes in the calibration curve.

3.3 Matrix spike (MS)—an aliquot of a sample to which known quantities of the analytes of interest are added. The MS is analyzed exactly like the samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. An MS is prepared for every batch of samples of a given matrix per day. Failure to meet criteria may be due to matrix interference within the sample. To be considered acceptable, MS must meet the in house % recovery criteria.

3.4 Matrix spike duplicate (MSD)—an additional aliquot of sample treated exactly as the MS. To be considered acceptable the RPD between the matrix spike sample and the matrix spike duplicate sample must meet the in house acceptance criteria and % recovery criteria as the MS.

3.5 Method blank (MB)—an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the lab environment, the reagents or the apparatus. A minimum of one MB per batch of samples, and is analyzed at the beginning of an analytical run. Blank recovery should be less than the MDL.

3.6 Linear calibration range (LR)—the concentration range over which the instrument response is linear. Samples with results greater than the highest calibration standard should be diluted to a concentration that falls within the calibration curve range and reanalyzed.

3.7 Method detection limit (MDL or LOD)—The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.8 Calibration Verification Standard-Initial (ICV) A midpoint calibration standard (10 ppm) which is analyzed after the calibration curve. The ICV must be from a second source different than that of the calibration standards,

3.9 Calibration Verification Standard-Continuing (CCV) - A midpoint calibration standard (10 ppm) which is analyzed at the beginning of the run, at a frequency of 1 per 10 samples during a run (CCV), and at the end of a run to verify calibration throughout the run. The CCV may be from the same source as the calibration standards.

3.10 Contract Required Detection Limit (CRDL or MRL) Standard--Detection level standard at a level near the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the CCB, and prior to the last CCV standard in the run.

3.11 Laboratory control sample (LCS) - is a 10 ppm standard made from the second source standard. It is run at the frequency of 1 per batch samples.

3.12 Batch- A batch consists of 20 samples of the same matrix analyzed on the same day or 20 samples of the same medium that have been prepared together.

4.0 HEALTH AND SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonable achievable.

4.2 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 The VFA samples have a 14 day holding time, unpreserved in a 40 ml VOA vial with no headspace.

5.2 Standards should be stored at 4° C (+/- 2 °).

6.0 INTERFERENCES

6.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used.

6.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms. Insure that all glassware is rinsed with Milli-Q water prior to use and use only Milli-Q water for making standards and reagents.

6.3 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. Care must be given when filtering samples to prevent the volatilization of the fatty acids.

6.4 The water dip or negative peak that elutes near, and can interfere with, the pyruvic peak. This is taken care of by adding 1% of the sample volume of eluent stock to the sample. I.e.) to a 5ml sample, add 0.050 ml of stock eluent acid (8.8.2).

7.0 PERSONNEL QUALIFICATIONS

7.1 Personnel operating the IC should have background knowledge of the scientific principles used during this application. All operators should perform an initial demonstration of capability (IDC) prior to analyzing any samples.

8.0 APPARATUS AND MATERIALS

8.1 Dionex DX-120 Ion chromatograph

8.1.1 Separator column, Dionex Ion Pac ICE-AS1 ,a column packed with a 7.5 um cross-linked styrene/divinylbenzene resin with sulfonate groups (9 x 250 mm, Dionex P/N 043197 or equivalent)

8.1.2 Regenerating suppressor, Dionex AMMS-ICE II, has a 4mm micro membrane Dionex P/N 037107 or equivalent)

8.1.3 Detector, a low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25 µL volume, Dionex DS4 or equivalent) equipped with a meter capable of reading from 0 to1,000 µseconds/cm on a linear scale.

8.1.4 Pump, capable of delivering a constant flow of 0.5 to 4 mL/min throughout the test.

8.1.5 Autosampler, Dionex AS40 with autosampler trays (Dionex P/N 046032 or equivalent), tubes and filter tops (Dionex P/N 038141 or equivalent).

8.1.6 Eluent reservoirs, suitable containers for storing eluent under pressure.

8.1.7 Computer with PeakNet 5.1 software and a printer, to integrate the area under the chromatogram. Software controls the DX-120 as well as processing and calculating data for the DX-120. Printer generates a paper copy of the data for archival purposes.

8.1.8 Bed support assembly- (Dionex P/N 048238 or equivalent)

8.2 Analytical balance, capable of weighing to the nearest 0.0001 g (Fisher Model A-200DS or equivalent).

8.3 Pipettes, Class A volumetric flasks, beakers: assorted sizes

8.4 Autopipettors of various volumes (Oxford Macro and Eppendorf micro)

8.5 Syringes (BD disposable or equivalent).

8.6 Glass Fiber Syringe Pre-Filters (Pall Acrodisc or equivalent).

8.7 0.45um Syringe filters with pre-filter (Whatman micro disc or equivalent).

8.8 Reagents

8.8.1 Reagent water--Milli-Q Deionized (DI) H2O

8.8.2 Eluent Concentrate—(0.1 M heptafluorobutyric acid, 99 %, Aldrich 164194-100g or equivalent). In a 1L volumetric flask, add 21.4 g of heptafluorobutyric acid and bring to volume with Milli-Q water.

8.8.3 Eluent—Use 10mL eluent concentrate (8.8.2) and bring to 1 liter with Milli-Q water. Helium purge to remove bubbles prior to use. Filter if necessary. Store on counter in IC lab.

8.8.4 Regenerate (anion suppression) – (5 mM tetrabutylammoniom hydroxide (TBAOH), dilute 50 mL of (0.1 M from Dionex #039602 or equivalent) to 1 liter with Milli-Q water. Or dilute 5 mL of (1.0 M from Aldrich #426326-100ml or equivalent) to 1 liter with Milli-Q water.

8.8.5 Stock Standards are purchased commercially and are used for the preparation of calibration standards, calibration check standards, and spiking standards.

8.8.5.1 Stock Acetic Acid -100%. Fisher, Cat. # F38-212 or equivalent. Store in metals department. Use manufactures expiration date.

8.8.5.2 Stock Butyric Acid – 99% Aldrich B103500-100ml or equivalent. Store in flammable cabinet. Use manufactures expiration date.

8.8.5.3 Stock Formic Acid – 96%. Sigma 251364-100g or equivalent. Store in flammable cabinet. Use manufactures expiration date.

8.8.5.4 Stock Lactic Acid - 85%. Sigma 252476-100g. Store in flammable cabinet. Use manufactures expiration date.

8.8.5.5 Stock Propionic Acid – 98%. Aldrich 107306-25g. Store in flammable cabinet. Use manufactures expiration date.

8.8.5.6 Stock Pyruvic Acid – 99.5% Sigma 402907-100ml. Store in flammable cabinet. Use manufactures expiration

8.8.5.7 Mixed stock standard (1000mg/L). Add 200 mL of Milli-Q water into a 500 ml volumetric flask. Weigh 0.500 g of acetic, butyric, formic, propionic and pyruvic acids the flask. Weigh 0.588 g of lactic acid into the same flask. Bring the volumetric flask to volume with Milli-Q water. Standard should be stored at 4 C for 6 months or as long as the integrity of the standard in kept intact. Standard is stored in the wet chem. refrigerator.

8.8.5.8 The ICV mix standard is made by a separate weighing of the standards from the same stocks as above.

8.8.5.9 All standards and preparations should be properly recorded in the wet chem. prep book and all bottles and containers properly labeled.

8.8.6 The calibration curves are brought to volume with Milli-Q DI H2O and are prepared as follows:

Stock Standard used	**ml of Stock Standard into 100 ml volumetric flask**						
	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7
Mix stock standard	0.1	0.2	0.5	1.0	2.5	5	10
Eluent conc. (8.8.2)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Calibration levels are	1ppm	2ppm	5ppm	10ppm	25ppm	50ppm	100ppm

100 ppm calibration standard is an optional standard, depending upon samples.

8.8.7 LCS/ICV (10 ppm) Mixed Standard—is made by diluting 1 ml of the stock mix standard 8.8.5.8, 1 ml eluent conc. (8.8.2) to 100 mL with Milli-Q water. Store in standards refrigerator in Wet Chem. lab. Standard expires after six months or sooner if stock solutions expire first.

8.8.8 CCV Mixed Standard - is made by diluting 1 ml of the stock mix standard 8.8.5.7, 1 ml eluent conc.(8.8.2) to 100 mL with Milli-Q water. Store in standards refrigerator in Wet Chem. lab. Standard expires after one month or sooner if stock solutions expire first.

8.8.9 All standards and preparations should be properly recorded in the wet chem. prep book and all bottles and containers properly labeled.

9.0 INSTRUMENT CALIBRATION

9.1 Start DX-120 and allow to equilibrate. See section 11.0 for further instructions on start up and method development.

9.2 In the PeakNet software, go to the Method Editor. Open a new file. See Section 11.3 for further instructions on method set-up.

9.2.1 Click on the Calibration Parameters icon.

9.2.1.1 Choose the General page. Choose the method of standardization to be external, the number of replicates is 1 the linear weighting is equal and the calibration standard volume is 1. Check the Replace Retention Time and Update Response/replace under the Update Data.

9.2.1.2 Choose the Defaults page. The sample volume, sample weight and dilution factor should all default to 1. The unknown response factor should default to 0 and the response for unknowns should default to area.

9.2.2 Click on the Component table icon.

9.2.2.1 On the Identification page:

9.2.2.1.1 The components for the anions group will elute in the following order: Fluoride, Chloride, Nitrite, Nitrate, *ortho*-Phosphate and Sulfate.

9.2.2.1.2 The retention times will be set based on the elution time of the analytes in a known standard. See method set up in Section 11.0 for further instructions.

9.2.2.1.3 For the Tolerance, choose 0.5 minutes.

9.2.2.1.4 For the Reference Component, choose none.

9.2.2.2 On the calibration Standards page:

9.2.2.2.1 The concentrations for each level in mg/L are:

	Cal. Level						
Compound	1	2	3	4	5	6	7
Pyruvic	1	2	5	10	25	50	100

Lactic	1	2	5	10	25	50	100
Formic	1	2	5	10	25	50	100
Acetic	1	2	5	10	25	50	100
Propionic	1	2	5	10	25	50	100
Butyric	1	2	5	10	25	50	100

On the Calibration page:

9.2.2.2.2 For the curve fit type, choose linear.

9.2.2.2.3 For the Origin, choose ignore

9.2.2.2.4 For Calibrate by, choose Area.

9.2.3 Save the method under C:\Instrument Archive\Method\System x\W####, where x is the system number and #### is the calibration standard number for the calibration curve.

9.3 Go to the Schedule Editor.

9.3.1 Under sample name, enter Level number. Repeat this for all eight levels.

9.3.2 Under the Sample type, choose calibration standard

9.3.3 Under Level, choose the appropriate level number for each level

9.3.4 Under the method name, choose the method just created (C:\instrument archive\method\system x\W####)

9.3.5 Under data file copy and paste the entries from the sample name column.

9.3.6 Save schedule under c:\instrument archive\schedule\system *\W####

9.4 Go to the Run Menu.

9.4.1 Go to file and choose load schedule.

9.4.1.1 Choose the schedule that you saved under c:\instrument archive\schedule\system *\W####

9.4.2 On the Sample page:

9.4.2.1 Under Data File, choose Browse.

9.4.2.2 Create a new directory under c:\instrument archive\data\system *. Name the new directory by the calibration standard number. Click OK

9.4.2.3 Under Data Collection, confirm that the defaults of DX-120 and the method run time appear.

9.4.3 On the Modes page:

9.4.3.1 Choose upon receiving signal at module.

9.5 On the AS-40 Autosampler:

9.5.1 Load the calibration standards in order.

9.5.2 Press the Run button to begin running.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 For acid, the samples should be collected unpreserved, holding time is 14 days in 40 ml VOA vials with no head space.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 Sample Preparation

11.1.1 For water samples, take 5 mL of sample and add 0.050 ml of eluent concentrate (8.8.2) to the sample. Put sample into an autosampler vial and cap with a filter cap.

11.2 Instrument equilibration

11.2.1 Turn on DX-120.

11.2.2 Ensure that Helium tank has an adequate supply of Helium for the run.
11.2.3 Fill the eluent containers on the top of the instrument with degassed eluent.
11.2.4 Turn on the Helium supply for the DX-120.
11.2.5 Press the Local/Remote button on the front of the DX-120. Make sure that the instrument screen on the front of the DX-120 says Local.
11.2.6 Press the Eluent pressure button. A green light should indicate that it is on.
11.2.7 Open the front cover of the instrument and locate the small screw, in the middle of the panel, that controls the purge for the pump.
11.2.8 Loosen the screw by turning 2 or 3 times
11.2.9 Press the pump button on the front of the instrument. A green light should indicate that it is on.
11.2.10 Allow the pump to prime for approximately one minute. If air is not purged from the system, increase the flow rate by pulling the knob adjacent to the pump and turning it clockwise. Turn the knob until the air is purged or until the flow rate is approximately 0.8mL/min. Allow the pump the prime for approximately one minute.
11.2.11 Close the pump screw
11.2.12 Press the SRS button on the front of the instrument. A green light should indicate that it is on. If the flow rate was increased to prime the pump return it to its original setting by turning the knob counterclockwise.
11.2.13 Maximum pressure is 1000 psi on the column.
11.2.14 Ensure there is enough regenerate in the 4 L bottle with enough degassed regenerate solution. Close bottle. Turn of pressure to the bottle to about 3 psi. This should produce a flow of 3 mL/min after about 10 minutes. Recommended flow is 3 – 5 ml/min.
11.2.15 Allow instrument to stabilize for 20-30 minutes prior to analysis.

11.3 Method creation in PeakNet software
11.3.1 Turn on computer
11.3.2 Open the PeakNet software by double clicking on the icon
11.3.3 Open the Method editor by left clicking on the Method icon.
11.3.4 Click on the new file icon (blank sheet) in the toolbar to open a new method file.
11.3.5 Highlight DX-120 under modules and then click add. Press Exit.
11.3.6 After the dialog box opens
11.3.6.1 Set the data collection time to 15 minutes.
11.3.6.2 Set the rate to 5.00 Hz
11.3.6.3 Set the Detector Unit to uS
11.3.6.4 Set the Plot Scales to 30.0 uS for the maximum and –3uS for the minimum.
11.3.6.5 Click on the timed events icon (stopwatch).
11.3.6.5.1 For time INIT, place a check mark next to TTL1. All others should be unchecked. Click enter.
11.3.6.5.2 For time 0.0, place a check mark next to offset. All others should be unchecked. Click enter.
11.3.6.5.3 For time 0.01, place a check mark next to begin. All others should be unchecked. Click enter.
11.3.6.5.4 Click exit.

11.3.6.6 Click on the integration icon (peak).
- 11.3.6.6.1 Set the Peak detection algorithm to standard
- 11.3.6.6.2 Set the peak width to 5-10 seconds.
- 11.3.6.6.3 Set the peak threshold to 0.2-0.25
- 11.3.6.6.4 Set the area reject to 1000
- 11.3.6.6.5 Set the reference area reject to 1000
- 11.3.6.6.6 Click OK

11.3.6.7 Click on the smoothing parameters icon.
- 11.3.6.7.1 Set the filter type to none.

11.3.6.8 Click on the data events icon (baseline)
- 11.3.6.8.1 Move the time line to the time that corresponds to the elution time of Fluoride (usually around 3 minutes).
- 11.3.6.8.2 Highlight the event option, void volume treatment for this peak.
- 11.3.6.8.3 Click add event
- 11.3.6.8.4 Click exit

11.3.6.9 For the calibration and component table icons, refer to section 9.0 to determine the correct settings.

11.3.6.10 Save the method as C:\INSTRUMENT ARCHIVE\METHOD\ SYSTEMx\ W####where x = the system number the method is for and the #### is for the W number of the standard prep.

11.3.6.11 Close the method editor.

NOTE: a calibration must be run for the method before it can be used to analyze samples. See Section 9.0 for further details.

11.4 Creating a schedule
- 11.4.1 Open the schedule editor by clicking on the icon.
- 11.4.2 A new file should appear. If not, click on the new file icon in the toolbar.
- 11.4.3 Under the sample column
  - 11.4.3.1 Type in the CTI sample ID for the sample to be analyzed. For DUP, MS and MSD samples, place the letters DUP, MS or MSD in front of the CTI sample ID.
  - 11.4.3.2 The first line in the schedule editor should be the CAL CHECK.
  - 11.4.3.3 The second line in the schedule editor should be ICV.
  - 11.4.3.4 The third line in the schedule editor should be ICB.
  - 11.4.3.5 After every ten samples and at the end of the run, a CCV, which is also used as an LCS, and CCB, which is also used as a MB, should be run.
- 11.4.4 Under the Method column, all lines should haveC:\ INSTRUMENT ARCHIVE\Method\System x\ W####.met, where W#### is the calibration standard number and x is the system number you are using.
- 11.4.5 Under the data file column, enter the same thing as the sample field. It is easier to copy and paste the sample column for this rather than hand entering all the information again.
- 11.4.6 Under the comments column, enter any dilution factors that you might have.
- 11.4.7 Save the schedule as c:\ INSTRUMENT ARCHIVE\Sequences\System X****** where x is the system number you are using and ****** is the LIMS run number.

11.4.8 Exit the schedule editor.

11.5 The run program in PeakNet
- 11.5.1 Click on the Run icon (center of screen)
- 11.5.2 Click on the window for the system you want to use.
- 11.5.3 Click on file. Choose Load Schedule.
  Select the schedule for that corresponds to the LIMS run number you want to run.
- 11.5.4 Click Open
- 11.5.5 Under data on the load schedule page
  - 11.5.5.1Click on browse
  - 11.5.5.2Double click on the folder under C:\instrument archive\data\system x
  - 11.5.5.3In the new directory box type in the LIMS run number that you want to run.
  - 11.5.5.4Click Create to create the file folder
  - 11.5.5.5Click OK to get back to the load schedule page
- 11.5.6 Under modes on the load schedule page
  - 11.5.6.1Click on the "upon receiving signal at module" button.
- 11.5.7 Click OK at the bottom of the Load Schedule page. The computer will be waiting for the autosampler to signal that a sample has been injected.

11.6 Load the autosampler with the samples in the order indicated in the schedule editor.

11.7 Press the Run/Hold button on the Autosampler. A green light will indicate that the autosampler is running.

11.8 To turn off the DX-120
- 11.8.1 Close the run in PeakNet
- 11.8.2 Close PeakNet software
- 11.8.3 On the DX-120:
  - 11.8.3.1Press the SRS button. The green light next to SRS should shut off.
  - 11.8.3.2Press the pump button. The green light next to pump should shut off.
  - 11.8.3.3Press the eluent pressure button. The green light next to the eluent pressure should shut off.

11.9 If system will remain off for an extended period of time
- 11.9.1 Press the button on the front of the DX-120 to turn off the power to it.
- 11.9.2 Turn off the power to the autosampler using the button on the left rear.

12.0 DATA CAPTURE

12.1 Select Batch in the PeakNet Main Menu.

12.2 Under File click open
- 12.2.1 Open C:\PeakNet\Schedule\DC.bch

12.3 Under Processing select Input
- 12.3.1 Click Select
  - 12.3.1.1Select the schedule you want to data capture. C:\Insturment Archive\ Schedule\System x***** where ***** is the LIMS run number.
  - 12.3.1.2Click Open
- 12.3.2 Process Injection should default to 1 through the last line of your schedule. If there are more than 100 lines in the schedule capture it in parts. For example when capturing a schedule that has 129 lines change the 129 to 100. Capture the schedule then repeat the process changing the 1 to 101 and leaving the 129.

12.3.3 Select All under included Detectors
12.3.4 Choose from schedule for process method
12.4 Under Output unselect all options.
12.5 Select Export
12.5.1 Change the file name to I:\DX120***** +.csv where ***** is the LIMS run number followed by +, an arbitrary letter. If capturing more than once to the same run, changing this letter prevents the files from being overwritten.
12.5.2 Select summary as the report type.
12.5.3 Choose Peak as the summary option.
12.6 Click OK
12.7 Click the Start Button
12.8 Exit the batch program. Do not save the changes.

13.0 TROUBLESHOOTING AND MAINTENANCE

13.1 See Dionex PeakNet Software User's Guide, Dionex DX-120 Operator's manual, Dionex Installation Instructions, Troubleshooting Guide for the ICE-AS1 and Troubleshooting Guide for troubleshooting instructions not covered in this section.
13.2 Iron contamination will cause a decrease in peak height. Successive injection of citric acid will remove the iron. Citric acid solution is a 5mM solution (0.096g of citric acid/100 ml Milli-Q water.
13.3 The column bed support assemblies should be replaced when they become clogged. A clog usually causes an increase in the pressure of the system. NOTE: DO NOT Replace the outlet bed support.
13.3.1 Disconnect the column from the system.
13.3.2 Carefully unscrew the inlet (top) column fitting. Use two open-end wrenches.
13.3.3 Remove the bed support. Turn the end fitting over and tap it against a bench top or other hard, flat surface to remove the bed support and seal assembly. If the bed support must be pried out of the end fitting, use a sharp pointed object such as a pair of tweezers, but be careful that you DO NOT SCRATCH THE WALLS OF THE END FITTING. Discard the old bed support assembly.
13.3.4 Place a new bed support assembly into the end fitting. Make sure that the end of the column tube is clean and free of any particulate matter so that it will properly seal against the bed support assembly. Use the end of the column to carefully start the bed support assembly into the end fitting. If the column tube end is not clean when inserted into the end fitting, particulate matter may obstruct a proper seal between the end of the column tube and the bed support assembly. If this is the case, additional tightening may not seal the column but instead damage the column tube or the end fitting.
13.3.5 Screw the end fitting back onto the column. Tighten it finger tight, then an additional 1/4 turn (25 in x lb). Tighten further only if leaks are observed.
13.3.6 Reconnect the column to the system and resume operation.
13.4 The column will need to be cleaned when the retention time window shift more than 10%, calibrations are no longer linear or the column becomes contaminated from a sample.
13.4.1 Prepare a 500 mL solution of 5 mM heptafluorobutyric acid in 10% acetonitrile. Make fresh as the acid decomposes the acetonitrile.

13.4.2 Disconnect the Amms-ICE from the IonPac ICE-AS1 Analytical Column. Direct the outlet flow to a waste container. Set the pump flow rate to 0.5 mL/min. Clean up will take about 60 minutes.

13.4.3 Reconnect the Amms-ICE back to the column.

13.4.4 Rinse the column for 30 minutes with eluent at 0.5 ml/min. Then return pump to normal pumping rate and equilibrate to 30 minutes before returning to normal operations

14.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

14.1 LIMS will calculate the following according to these equations:

14.1.1 *Liquid Concentration (mg/L)* = A x C

Where A = instrument reading for sample (mg/L)
C= dilution factor

14.1.3 $Spike\ Recovery\ (\%) = \frac{(\text{Spiked sample value} - \text{Sample value}) \times 100}{(\text{Spike amount})}$

14.1.4 $\%RSD = \frac{|(\text{Sample} - \text{DUP})| \times 100,}{(\text{Sample} + \text{DUP})/2}$

where DUP = Duplicate concentration

15.0 COMPUTER HARDWARE AND SOFTWARE

15.1 Computer with LIMS

15.2 Printer (Hewlett Packard, Model-Laserjet 4000)

15.3 PeakNet 5.0 Software (also see 11.3 Method Creation)

15.3.1 Absolute retention times for targeted compounds are determined by the Initial Calibration and the Continuing Calibration Verification standards analyzed prior to sample analyses. Retention Time Windows (RTW) are used to determine peak ID.

15.3.2 Peak widths settings can help identify the proper peaks, as well as, ensure proper integration. Depending on a given analytes response the peak width are set at 5 to 10 %, based on the absolute retention times of a given peak.

15.3.3 Peak thresholds depend on a given instruments response and are currently set at 0.2 (system 1). Setting the thresholds to low can make it difficult to distinguish peak response from baseline noise.

15.3.4 Area reject is also set according instrument response. Currently the area rejects (both systems) are set at 1000 area counts. Setting the area counts to high is a problem because low level detects can be missed; but setting the area reject to low will again introduce problems with baseline noise. MDL study results are a helpful tool in determining area reject values, as well as, threshold values.

15.3.5 A properly integrated peak should be integrated from the start of the peak to the end of the peak (valley to valley) and should not include any area between peaks or areas that are below the baseline. Refer to the facilities SOP (SS-10, Rev. 1) on Manual integrations when it appears that peaks may be improperly integrated.

Follow the proper documented procedures before using any manual integration tools.

15.3.5.1 There are other features/function included in the software that can help with peak identity, instrument sensitivity, and proper integrations. Refer to the Software's users guide (sections 10.4.2, 10.4.3, and 10.4.4) for definitions and prior use.

16.0 DATA MANAGEMENT AND RECORD MANAGEMENT

16.1 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist for data review guidance.

16.2 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

16.3 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

16.4 The original data is filed by test in the file cabinet and periodically the contents of the file cabinet are archived.

17.0 QUALITY CONTROL AND QUALITY ASSURANCE

17.1 At the beginning of a run and after every 10 samples analyze a midrange calibration standard (CCV@10 ppm). If the instrument retention time has changed by more than 10% or recovery is outside of 80-120%, remake solution and analyze the fresh solution. If it still does not fall within the above criteria, recalibrate.

17.2 A matrix spiked (MS)sample and matrix spike duplicate (MSD) should be run for each analytical batch or twenty samples for to determine matrix effects. The matrix spice is made by using 5 ml of sample and adding 0.050 ml of mix standard (8.8.5.7) and 0.050 ml of eluent concentrate (8.8.2). Recoveries should be between 70-130%/20%RPD or within in-house or program specific limits.

17.3 Prior to analyzing samples, each analyst must perform an IDC, initial demonstration of capability. The IDC consists of running a standard solution in quadruplicate and getting a recovery and RPD within method limits.

17.4 Method Detection Limit (MDL)—MDLs must be established for all analytes, using reagent water fortified at a concentration of 3-5 times the estimated instrument detection limit. To determine MDL values, take seven or eight replicate aliquots of the fortified reagent water and process through the entire analytical method. Calculate the MDL using the spreadsheet in H:\MDLs\classical\MDL water blank workbook.xls for waters of h:\MDLs\classical\MDL soil blank workbook.xls for soils. MDLs should be determined annually or whenever there is a significant change in background or instrument response.

17.5 Calibration Blank (CB)—a volume of reagent water fortified with the same matrix as the calibration standards. It is analyzed immediately following the calibration standards (Initial Calibration Blank-ICB), at a frequency of 1 per 10 samples during a run (Continuing Calibration Blank-CCB), and at the end of a run to check for drifts in calibration, or possible analyte carry-over. Control criteria consist of the absolute value being less than the MDL for a given analyte. If this range is exceeded, reanalyze, and if still exceeding a new calibration will be necessary or data flagged appropriately.

17.6 Laboratory Control Sample (LCS) is a 10 ppm standard made from a second source and is run once in every 20 samples to confirm the standard curve. Recovery should be between 70 – 130 % or with in-house generated or program specific limits.

17.7 Method Blank (MB)—a volume of reagent water fortified with the same matrix as the calibration standards. It is analyzed following the CCV at a frequency of 1 per 20 samples during a run. Control criteria consist of the absolute value being less than the MDL for a given analyte. If this range is exceeded, reanalysis of samples may be necessary or data flagged appropriately.

18.0 References

18.1 Dionex Product manual for the IonPac ICE-AS1, Document # 031181, Revision 7, June 19, 2006

18.2 DX-120 Ion Chromatograph Operator's Manual, Dionex, Document No. 031183, Revision 03, September, 1998.

18.3 PeakNet Software User's Guide, Dionex, Document No. 034914, Revision 09, June, 2000.

18.4 DX-120/100 Maintenance & Troubleshooting, Training Course Manual, Dionex, Document No. 031399, Revision 01, 1998

Standard Quality Control Requirements and Corrective Action Guidelines

QC Type	Frequency	Conc. Level	*Acceptance Criteria*	*Corrective Action*
ICAL	As needed		R $\geq$ 0.995	Recalibrate Instrument
ICV	1 per calibration	Midpoint of cal curve	80-120%	Reanalyze or recalibrate
ICB	1 per calibration		<LOD	Correct problem and reanalyze
CCV	1 after every 10 samples	Midpoint of cal curve	80-120%	Correct problem and reanalyze.
MB	One per batch (up to 20 samples)		< LOD or program/project specific	Correct problem and reanalyze or qualify data (B) that is not > 20 times the MB or <LOD
CCB	Following each CCV except when MB analyzed after CCV		<LOD	Correct problem and reanalyze or qualify data (B) that is not > 20 times the ICB or <LOD
LCS	1 per batch of 20 samples	Midpoint of cal curve	In-house generated or program / project specific limits Default: 70-130 %	Correct problem and reanalyze. If reanalysis fails reanalyze complete batch. Data reported with failing LCS must be qualified (Q).
DUP	5% (1 for every 20 samples) per matrix		In-house or project/program specific limits. Default is 20% Diff. A matrix spice duplicate may be used instead	Identify source of problem. Qualify data (Y) or reanalyze depending on source of problem.
MS and/or MSD (MSD=QSM requirement)	5% (1 in 20) of samples per batch per matrix		In-house or program/project specific limits. Default limits are 70-130%	Identify source of problem. Qualify data or reanalyze depending on source of problem.

Data Validation Checklist

LIMS #:	Method: Volatile Fatty Acids by Ion Chromatography			
Analysis Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were the samples analyzed within hold time?	14 days, unpreserved in 40 ml VOA without head space					
2. Was the calibration performed using the required number of standards?	Minimum 5 plus a blank					
3. Is the standard prep log number noted on the analytical report?	---					
4. Was the correlation coefficient acceptable?	>= 0.995					
5. Were the ICV and ICB run immediately after the calibration check standard?	---					
6. Was the ICV recovery acceptable?	80 – 120 %					
7. Was the ICB result acceptable?	< LOD					
8. Were the CCV's and the CCB's analyzed at the required frequency?	1per 20 samples					
9. Were the CCV recoveries acceptable?	80 – 120 %					
10. Were the CCB results acceptable?	< LOD					
11. Was the MB analyzed at the required frequency?	1 per 20 samples					
12. Were the MB results acceptable?	< LOD or program/project specific					
13. Was a LCS run at the required frequency?	1 per 20 samples					

15. Was the LCS recovery acceptable?	In-house or program/project specific Default 70-130%					
16. Was the LCS used before the indicated expiration date?	---					
17. Were the MS and MSD prepared at the required frequency (MSD for QSM Data)?	1per 20 samples per matrices					
18. Were the MS and MSD recoveries acceptable?	Within In-house or program/project specific limits. Default 70-130%					
19. Was the RPD between the MS and MSD acceptable?	Within in house or program/project specific limits Default 20%					
20. Was a sample duplicate prepared at the required frequency?	Program/Project specific or 1 per 20 samples					
21. Was the duplicate within precision limits?	In-house or program/project specific. Default 20%					
22. Were all chromatograms checked to ensure accurate peak identification?	---					
23. Are all samples on the job lists accounted for?	---					

MEMORANDUM **SMF-4J**

DATE: February 15, 2007

SUBJECT: Approval of the First Revision Supplemental Quality Assurance Project Plan (QAPP) for the Fund-Lead Remedial Investigation/Feasibility Study (RI/FS) Pilot Study Test at the **OMC Plant 2 Site** in Waukegan, Illinois

FROM: Richard L Byvik Richard L Byvik
Field Services Section (FSS)

TO: Kevin Adler
Remedial Project Manager (RPM)

I recommend approval of the first revision Supplemental QAPP for the Fund-Lead RI/FS Pilot Study Test at the **OMC Plant 2 Site** in Waukegan, Illinois. The subject QAPP was received by FSS on January 22, 2007, Log-in # 3469. The Signature page has been signed and returned with the subject QAPP to the RPM.

CC: Steve Ostrodka

SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN
OMC Plant 2
Waukegan, Illinois
RI/FS – Pilot Testing
WA No. 018-RICO-0528 / Contract EP-S5-06-01

Prepared by: CH2M HILL Date: December 2006

Approved by:

USEPA, Region 5, Work Assignment Manager
Kevin Adler

2/15/07
USEPA, Region 5, Quality Assurance Reviewer

CH2M HILL Site Manager
Jewelle Keiser

CH2M HILL Quality Assurance Manager
Regina Bayer

CT Laboratories Quality Assurance Manager (TBD)

Response to USEPA's QAPP and FSP Comments OMC Plant 2 RI/FS, Pilot Testing, Waukegan, Illinois WA No. 018-RICO-0528, Contract No. EP-S5-06-01

TO: Kevin Adler/USEPA

COPIES: Phil Smith/CH2M HILL
Paul Rohde/CH2M HILL

FROM: Steve Paukner/CH2M HILL
Jewelle Keiser/CH2M HILL

DATE: January 15, 2007

PROJECT NUMBER: 348138.PP.02

We have reviewed your comments (dated November 8, 2006) on the *Supplemental Field Sampling Plan* (SFSP) and the *Supplemental Quality Assurance Project Plan* (SQAPP) for the pilot study test at the OMC Plant 2 site in Waukegan, Illinois. The following responses (in *italics*) to comments indicate how each comment was addressed in the revised plans.

Supplemental Quality Assurance Project Plan

A. TITLE/APPROVAL PAGE

Identify the offsite laboratory/laboratories performing the analytical work and include signature lines. Is CT Laboratories (CTL) still the offsite laboratory?

CT Laboratories will be the laboratory performing the work and was added to the signature line.

B. Element 1.3 and Table 1

The Method OLC03.2 has been replaced with the new CLP SOW SOM01.1 Trace Volatiles (Trace VOA) method.

Method OLC03.2 has been replaced with CLP SOW SOM01.1 in Table 1.

Please verify if the project requires analysis for the Parameters Dichlorofluoromethane (Freon 21) and 1,3-Dichloropropane. These 2 Parameters are not included in the Volatiles Target Compound List for SOM01.1 Trace VOA method. The CLP laboratories will have to be instructed to include these 2 Parameters.

Dichlorofluoromethane and 1,3-Dichloropropane were not included in the analyte list. These compounds were not detected during the previous investigations.

C. Element 2.4

Identify the offsite laboratory/laboratories. If another offsite lab is selected, not CTL, that lab must provide Standard Operating Procedures (SOPs).

CTL has been selected as the subcontracted offsite laboratory.

Denote the laboratory that will be analyzing for the Parameter Volatile Fatty Acids (VFAs). Itemize the VFAs and the project required Reporting Limits. If CTL will be analyzing for VFAs, CTL must provide an SOP, method detection limits and method reporting limits for VFAs.

The SOP for VFAs has been finalized by CTL and has been included with the final SQAPP. The following itemized VFAs and reporting limits were specified in the laboratory scope of work with CTL.

Parameter	*LOD/MDL (mg/L)*	*LOQ/PQL (mg/L)*
Pyruvic Acid	*0.8*	*2.6*
Lactic Acid	*0.7*	*2.2*
Formic Acid	*0.6*	*1.4*
Acetic Acid	*0.5*	*1.7*
Propionic Acid	*0.5*	*1.8*
Butyric Acid	*0.5*	*2.0*

D. Element 4.1

The USEPA CLP National Functional Guidelines for Organic Data Review (October 1999) has been replaced with Draft Final USEPA CLP National Functional Guidelines for Superfund Organic Methods Data Review January 2005.

This has been corrected to show the most recent version (2005).

E. Tables

In all the tables replace OLC03.2 with SOM01.1 Trace VOA Method. Likewise, in all tables replace OLM04.2/OLM04.3 with SOM01.1 Low/Medium VOA Method for soils and water.

Tables have been revised by replacing OLC03.2 with SOM01.1.

F. TABLE 6

Include the container, preservation, and holding time requirements for VFAs.

Table 6 has been revised to include the container, preservation, and holding times for VFAs.

SUPPLEMENTAL FIELD SAMPLING PLAN

A. Section 2.2.1, TABLE 2-1, and TABLE 2-7

Provide an SOP for the field measurements of Ferrous Iron and Total Iron on soil samples. Are these field measurements considered qualitative or quantitative?

The FOP for the field measurements of iron was inadvertently left out of the revised document and has been attached.

B. Section 2.2.3

Delete reference to "Contract Laboratory Analytical Services Support (CLASS) personnel." CLASS no longer exists.

The reference has been deleted.

C. Section 2.2.4

See Supplemental QAPP Comment C above.

Comment noted.

D. Section 3.2.4.4

Verify reference to Table 2-5.

The reference to Table 2-5 is correct.

The reference to Table 2-6, perhaps, should be Table 2-1.

The reference to Table 2-6 has been revised to Table 2-1.

E. Tables

In all the tables replace OLC03.2 with SOM01.1 Trace VOA Method. Likewise, in all tables replace OLM04.2/OLM04.3 with SOM01.1 Low/Medium VOA Method for soils and water.

The tables have been revised to refer to method SOM01.1.

F. TABLE 2-2

See Supplemental QAPP Comment B above.

Dichlorofluoromethane and 1,3-Dichloropropane were not included in the analyte list. These compounds were not detected during the previous investigations.

FIELD OPERATING PROCEDURE FOP-23

Soil Mixing Iron Extraction Method

Purpose

The purpose of this FOP is to present the protocols for extracting zero-valent iron (ZVI) from soil treated using in-situ soil mixing with bentonite clay and ZVI.

Scope

The method described for iron extraction is applicable for soils treated by incorporating bentonite clay and ZVI.

Equipment and Materials

- 4 to 8 ounces of treated soil
- Two clean, unpreserved, 4-ounce glass jars
- Small ferrous iron pan
- Small oven (toaster oven or equivalent capable of holding small ferrous iron pan)
- Digital scale capable of measuring to 0.1 grams
- 2 small disposable plastic spoons
- Distilled water
- Paper towels
- Wax paper
- Spray bottle
- Large magnet (e.g., 6-inch speaker magnet)
- Plastic food wrap
- Pencil
- Field logbook and camera
- 5-gallon bucket
- Decontamination supplies
- Protective equipment, including heat-resistant outer gloves, nitrile gloves, safety glasses, and dust mask (Note: See HSP for specific PPE required for the sampling activities.)

Procedures and Guidelines

1. Decontaminate the large magnet and ferrous iron pan using the methods specified in FOP-18 (Decontamination of personnel and equipment).
2. Place a clean 4-ounce glass jar on the digital scale and press tare.
3. Weigh out 50 - 100 grams of treated soil into the jar.
4. Record the wet sample weight of the soil in the field notebook.

5. Transfer the soil onto the decontaminated ferrous iron pan and place the pan into the oven on low to moderate heat until the soil is complete dry. **Do not leave oven unattended while operating.**
6. Place a clean 4-ounce glass jar on the digital scale and press tare.
7. After soil is completely dry carefully transfer the dried soil into the clean 4-ounce jar.
8. Record dry sample weight in the field notebook.
9. Calculate iron concentration by placing a clean, unpreserved, 4-ounce glass jar on digital scale and tare.
10. Carefully weigh out 50 - 100 grams of treated soil into the clean, unpreserved, 4-ounce glass jar and record soil weight in field notebook.
11. Transfer the soil onto the decontaminated ferrous iron pan.
12. Fill spray bottle with distilled water.
13. Carefully wet and agitate soil in pan to suspend fine-grained soil and clay in water.
14. Decant rinse water with suspended fine-grained material into 5-gallon bucket **while retaining iron and coarse soil (sand) particles.** Repeat steps 13 and 14 twice.
15. Place the large magnet on the **underside** of the pan.
16. Add more water and slowly move slurry across the magnet to allow iron particles to accumulate in the pan directly above the magnet.
17. Transfer rinse water, iron, and soil (this is the "iron sand concentrate") that have not accumulated above the magnet into a clean container.
18. Remove iron that has accumulated above the magnet and place into a clean, 4-ounce glass jar.
19. Return the "iron sand concentrate" to the pan and repeat steps 16 through 18 until the remaining sand is visibly free of iron particles.
20. Remove large magnet from the base of the pan.
21. Place pan with iron in the oven on low to medium heat until the iron is dry.
22. Turn off heat and allow pan to cool.
23. To remove any remaining sand, spread the dried iron thinly on a clean piece of wax paper.
24. Cut one piece of plastic wrap large enough to cover the magnet
25. Weigh the two pieces of plastic wrap on the scale and record the weight in the field notebook. Wrap the magnet in the plastic wrap.
26. Collect iron particles by passing the magnet over the material on the wax paper. Care should be taken not to pick up soil particles with the magnet.

27. Carefully remove the plastic wrap from the magnet, fold the plastic wrap to contain the iron, and weight the plastic wrap and iron.
28. Subtract the weight of the plastic wrap from the iron - plastic wrap combination.
29. Calculate the iron fraction per dry weight soil using the following formula:

$$\%Iron = \frac{WeightExtractedIron}{InitalSampleWeight\frac{DrySampleWeight}{WetSampleWeight}} * 100$$

Attachments

None.

Key Checks and Items

- Ensure consistent application of the procedure between sampling locations
- Consider preparation of a known concentration standard to determine potential margin of error.
- Run standard mixture multiple times to optimize process layout.